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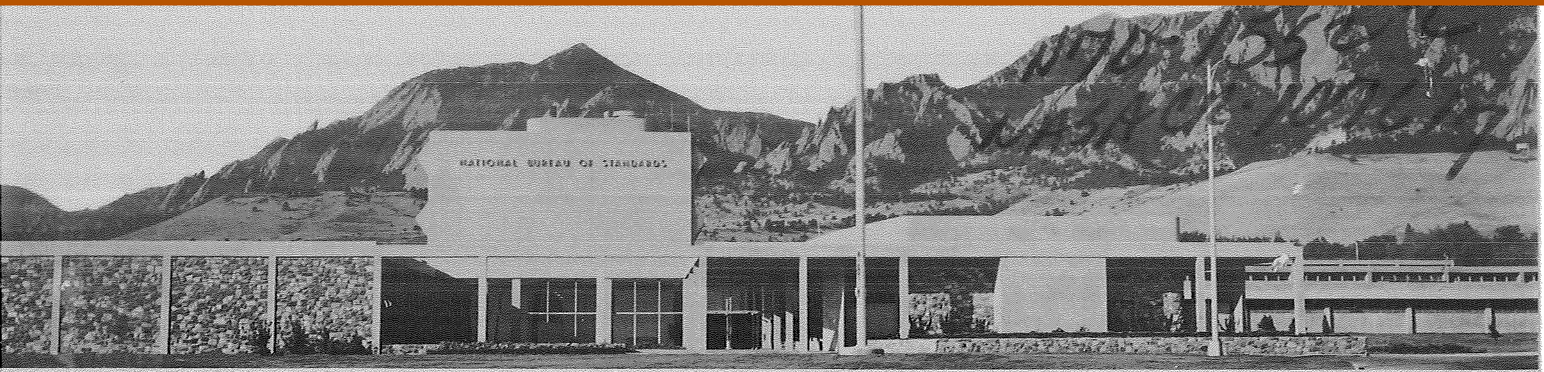

NBS REPORT

9733 NI

NATURAL GAS AND METHANE

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by

D. B. Mann and W. J. Hall

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NATURAL GAS AND METHANE*

by

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NATURAL GAS AND METHANE

D. B. Mann and W. J. Hall

ABSTRACT

The terms methane and "natural gas" cannot be used interchangeably. Analysis of available data shows that the variation in constituents of natural gas is significant and must be considered when projecting wide spread use of this energy source in liquefied form.

Spectrographic data for natural gas mixtures analyzed for hydrogen, helium, methane, nitrogen, ethane, oxygen, hydrogen sulfide, argon, carbon dioxide, propane, n-butane, isobutane, n-pentane, isopentane, cyclopentane, and hexanes are grouped as to sample source. Maximum and minimum variations in constituents are presented to show the broad range of mixtures possible in the natural gas.

Key Words: Gas analysis, liquefied natural gas, methane, natural gas.

1. Study Objectives

The introduction and use of liquefied natural gas (LNG) as an energy source for public and private utilities, as well as substitute fuel for internal combustion engines, has grown significantly over the last five to ten years. The projected use of LNG or methane as a fuel for the supersonic transport (SST) is only one of the most recent applications of this energy source. This increasing and widespread use of liquefied natural gas has generated an interest in the basic thermophysical properties of the fluid. Since the raw material for liquefied natural gas is a mixture of many gaseous substances in varying proportions, there has resulted quite naturally, some confusion in the resulting properties of the liquefied fluid. Even though the terms liquefied natural gas and liquid methane are often used interchangeably, LNG contains several constituents in addition to its major one, methane.

It is the objective of this study to present data on the composition of natural gas from various sources in such a way as to indicate the variable make-up of the raw gas used to make liquefied natural gas. An appreciation of the variability is necessary in assessing the advantages of liquefied natural gas as an energy source. The presence of natural gas is reasonably well distributed throughout the world. To take advantage of this fact and utilize this energy source in a liquid form requires a knowledge of the properties of the mixtures of the various components after the natural gas has been liquefied. The tacit assumption that liquefied natural gas in general has the properties of liquid methane has not been established. Even during the liquefaction process itself, the makeup of the natural gas must be known in order to eliminate higher freezing point constituents which could ultimately interfere with the liquefaction process.

It is, therefore, the objective of this study to show the constituents of natural gas, indicate their extent, and to show the variations in gas composition, if any, as a function of the source gas.

A study of the constituents of natural gas was made possible by the extensive sample analysis program conducted by the U. S. Department of the Interior, Bureau of Mines. Since helium is found in economically recoverable quantities in natural gas, the Helium Activity of the Bureau of Mines has conducted, during a period of over fifty years, a program of sampling natural gases for the determination of the presence of helium. This sampling program was initiated in 1917 and is continuing at the present time. Over 7500 gas samples have been taken and analyzed and the results published [1-9].

The Bureau of Mines has made recently available, on computer card format, 923 samples and analyses roughly covering the period from 1964 to 1967. This information is the basis for the following presentation. The most recent grouping of gas samples is based on source. These are samples from domestic oil and gas wells, from domestic pipelines, from foreign oil and gas wells, and from foreign pipelines. Original sample analysis was conducted using an Orsat method, but this has been replaced with mass spectrometer techniques. Samples are analyzed for hydrogen, carbon dioxide, propane, n-butane, isobutane, n-pentane, isopentane, cyclopentane, and heavier hydrocarbons of the molecular weight of hexane or greater. Although many of these constituents will not effect liquefaction of the natural gas, the effect of these constituents on the properties of liquefied natural gas has not been determined. It is an additional purpose of this study to show that these constituents must be contended with and either eliminated prior to liquefaction or dealt with in a liquid state.

2. Natural Gas from Domestic Oil and Gas Wells

The greatest portion of samples considered lie in this grouping. Eight-hundred and thirty-nine samples were analyzed, roughly through the period of 1964 to 1967. Since, in most cases, the primary constituent of natural gas is methane, this fact has been used in establishing a method of data presentation. Tables 1 and 2 and figure 1 summarize the data while table 3 shows the variation of constituents within the ten percentile methane grouping having the greatest number of samples.

3. Domestic Pipelines

The Bureau of Mines survey includes 25 domestic pipeline samples taken over a period from March 1966 to September 1967. It is assumed that this gas is being transported as an energy source. The heating value ranges from 953 to 1384 Btu's per cubic foot at 60°F and 30 inches of mercury.

A summary of these data appear in tables 4 and 5 and figure 2. The variation of the constituents is much less than in the case of domestic oil and gas wells and it is evident that this gas has been treated to give a certain range of heating values. A range of constituents for a 10 percent variation in methane content, containing also the greatest number of samples, is presented in table 6. The variation in constituents, even with the restriction, is still quite marked.

4. Foreign Oil and Gas Wells

Data on foreign oil and gas wells have been included in the Bureau of Mines analysis since the latter part of 1965. A summary of 22 samples is shown in tables 7 and 8 and figure 3. Again, as in the case of domestic oil and gas wells, there is an extremely broad range of composition.

Table 1

Domestic Oil and Gas Wells

Geographical Distribution

Location	Number
Alaska	3
Arizona	3
Arkansas	18
California	10
Colorado	14
Indiana	1
Kansas	85
Kentucky	19
Louisiana	8
Maryland	1
Michigan	4
Mississippi	1
Montana	8
Nebraska	4
New Mexico	44
New York	12
North Dakota	15
Ohio	51
Oklahoma	168
Pennsylvania	99
Texas	191
Utah	16
Virginia	14
West Virginia	29
Wyoming	21

Table 2

Domestic Oil and Gas Wells - Summary

839 Samples

Gas (Increasing mole wt.)	Minimum mole %	Maximum mole %	Number of Samples Present
Hydrogen	Trace	6.6	111
Helium	Trace	11.1	838
Methane	Trace	99.1	all
Nitrogen	Trace	99.4	832
Ethane	Trace	44.3	829
Oxygen	Trace	0.7	255
Hydrogen Sulfide	0.1	3.7	8
Argon	Trace	1.0	639
Carbon Dioxide	Trace	96.0	789
Propane	Trace	35.2	803
n-Butane	Trace	12.5	717
Isobutane	Trace	4.6	685
n-Pentane	Trace	3.2	684
Isopentane	Trace	2.9	679
Cyclopentane	Trace	1.0	691
Hexanes +	Trace	3.2	691

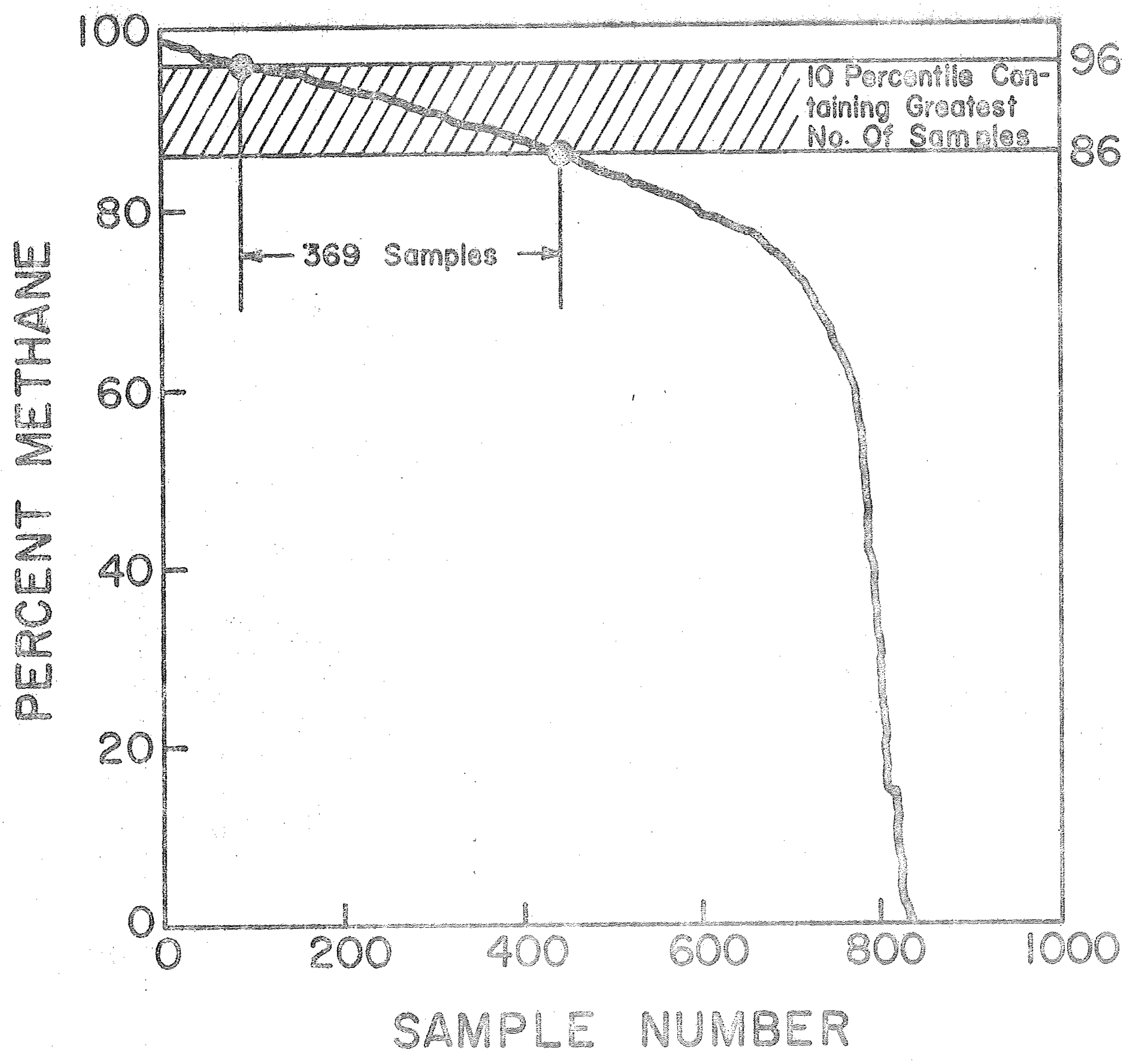

Figure 1. Domestic Oil and Gas Wells - Samples Ordered as to Methane Content.

Table 3

Domestic Oil and Gas Wells

Range of Constituents for 369 Samples Having 86 - 96% Methane*

Gas (Increasing mole wt.)	Minimum mole %	Maximum mole %	Number of Samples Present
Hydrogen	Trace	0.6	40
Helium	Trace	0.71	368
Methane	86.0	96.0	all
Nitrogen	Trace	12.1	361
Ethane	0.1	9.2	368
Oxygen	Trace	0.7	111
Hydrogen Sulfide	0.0	0.0	none
Argon	Trace	0.1	287
Carbon Dioxide	Trace	10.3	342
Propane	Trace	3.8	363
n-Butane	Trace	1.3	328
Isobutane	Trace	1.2	252
n-Pentane	0.1	1.0	309
Isopentane	Trace	1.4	306
Cyclopentane	Trace	0.7	314
Hexanes +	Trace	1.1	314

* This ten percentile contains the greatest number of samples (44%).

Table 4

Domestic Pipelines

Geographical Distribution

Location	Number
Kansas	2
North Dakota	2
Ohio	9
Pennsylvania	2
Texas	10

Table 5

Domestic Pipelines - Summary

25 Samples

Gas (Increasing mole wt.)	Minimum mole %	Maximum mole %	Number of Samples Present
Hydrgoen	Trace	0. 1	9
Helium	Trace	0. 64	all
Methane	66. 1	87. 7	all
Nitrogen	0. 5	15. 3	all
Ethane	5. 2	16. 8	all
Oxygen	Trace	0. 4	7
Hydrogen Sulfide	0. 2	1. 1	2
Argon	Trace	0. 1	19
Carbon Dioxide	0. 1	2. 6	21
Propane	1. 0	8. 0	all
n-Butane	Trace	2. 8	all
Isobutane	Trace	1. 3	all
n-Pentane	Trace	0. 9	24
Isopentane	Trace	0. 9	all
Cyclopentane	Trace	0. 3	all
Hexanes +	Trace	0. 8	all

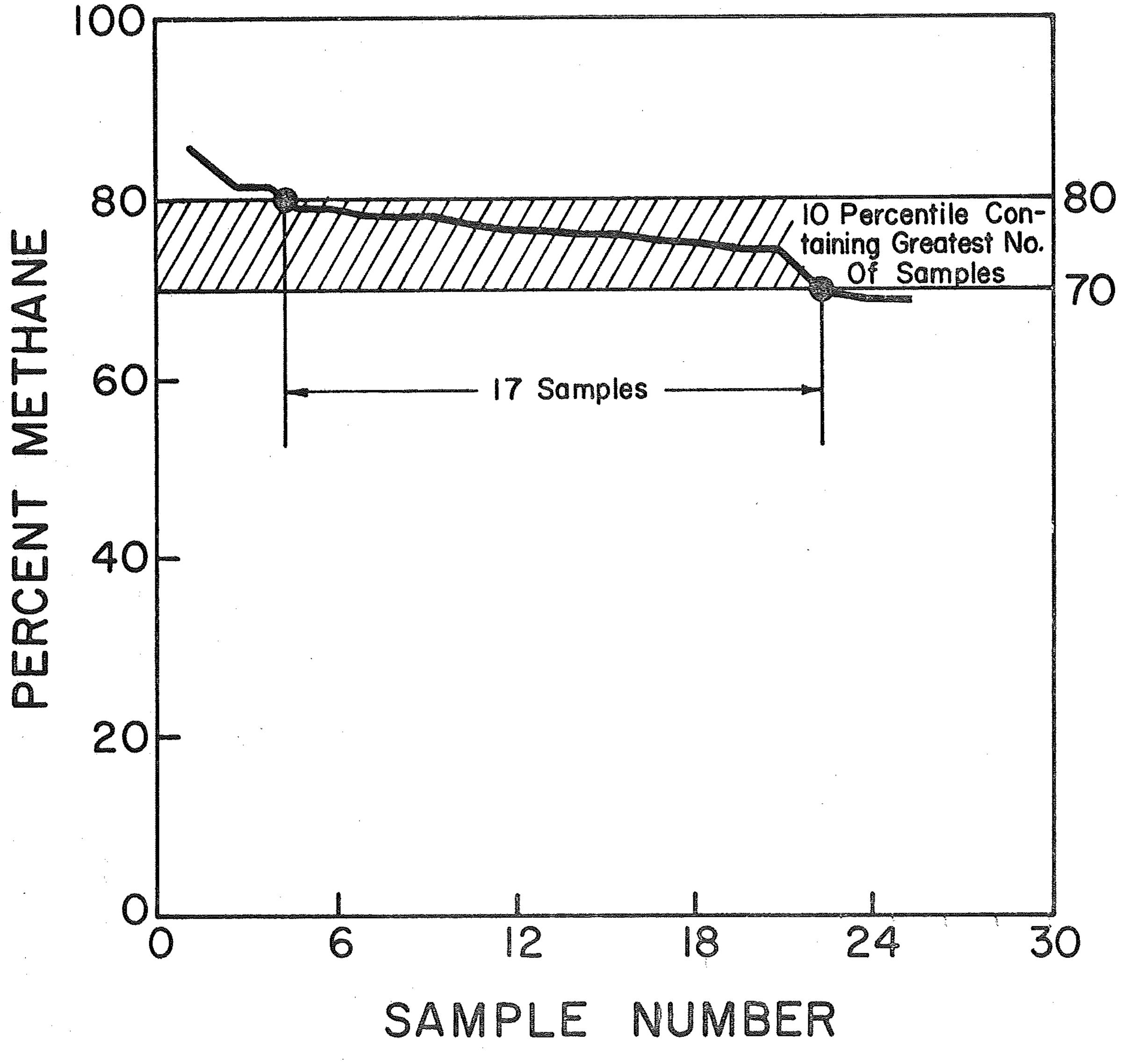

Figure 2. Domestic Pipelines - Samples Ordered as to Methane Content.

Table 6

Domestic Pipelines

Range of Constituents for 17 Samples Having 70 - 80% Methane*

Gas (Increasing mole wt.)	Minimum mole %	Maximum mole %	Number of Samples Present
Hydrogen	Trace	Trace	7
Helium	0.1	0.64	all
Methane	70.0	80.0	all
Nitrogen	1.8	15.3	all
Ethane	5.3	16.5	all
Oxygen	Trace	0.1	4
Hydrogen Sulfide	none	none	none
Argon	Trace	0.1	14
Carbon Dioxide	0.1	0.5	13
Propane	1.0	6.2	all
n-Butane	Trace	2.4	all
Isobutane	Trace	0.9	all
n-Pentane	Trace	0.7	16
Isopentane	Trace	0.7	all
Cyclopentane	Trace	0.2	all
Hexanes +	Trace	0.5	all

* This ten percentile contains the greatest number of samples (68%).

Table 7

Foreign Oil and Gas Wells

Geographical Distribution

Location	Number
Australia	1
Bolivia	5
Canada	8
Netherlands	8

Table 8

Foreign Oil and Gas Wells - Summary

22 Samples

Gas (Increasing mole wt.)	Minimum mole %	Maximum mole %	Number of Samples Present
Hydrogen	Trace	0.2	5
Helium	Trace	1.2	all
Methane	1.7	96.2	all
Nitrogen	0.5	96.6	all
Ethane	0.1	8.9	21
Oxygen	Trace	0.4	11
Hydrogen Sulfide	Trace	Trace	1
Argon	Trace	0.2	13
Carbon Dioxide	Trace	4.3	20
Propane	0.1	4.0	13
n-Butane	0.2	1.4	16
Isobutane	Trace	1.1	16
n-Pentane	0.1	0.8	16
Isopentane	Trace	0.5	16
Cyclopentane	Trace	0.4	16
Hexanes +	0.2	1.7	16

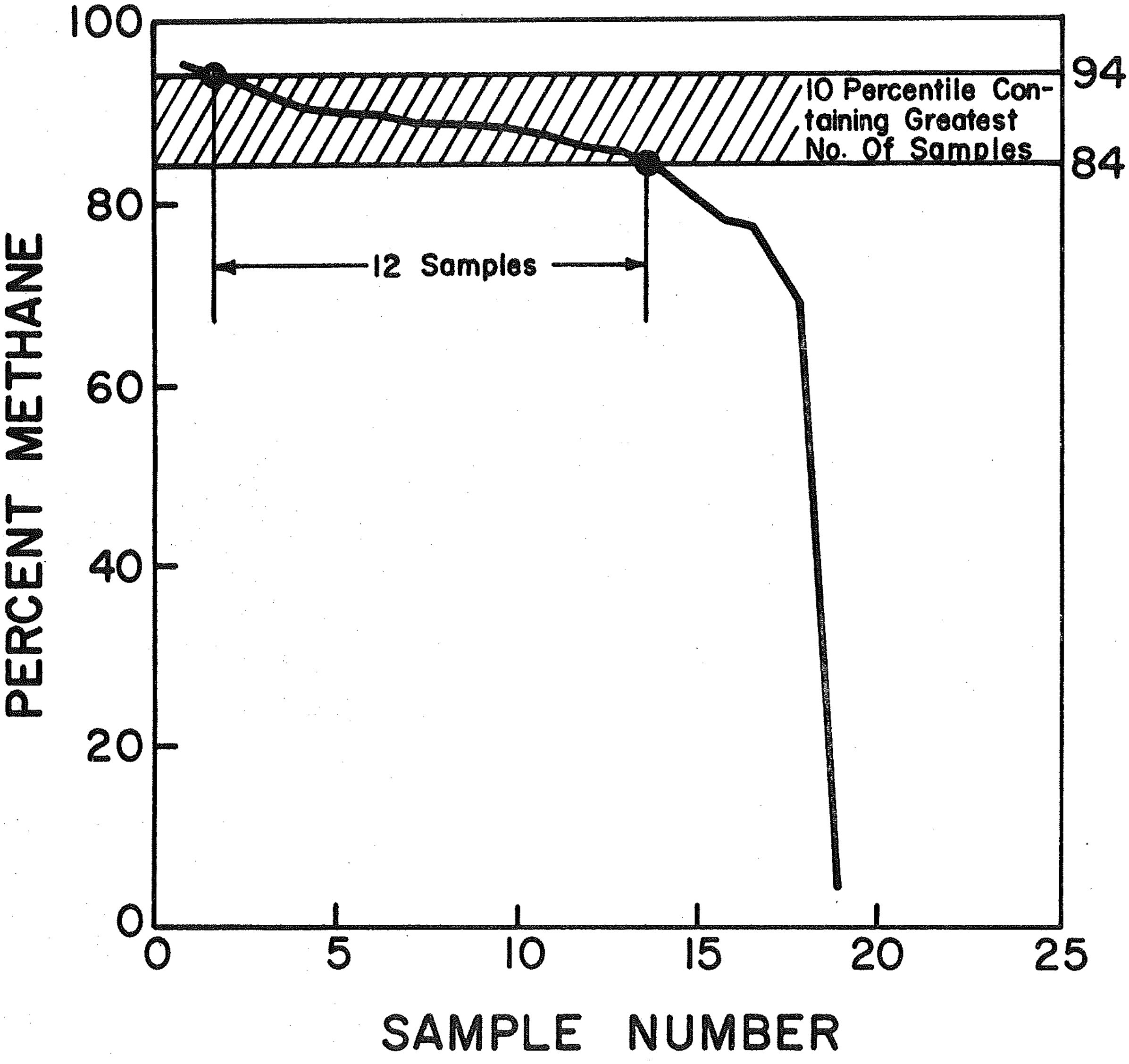

Figure 3. Foreign Oil and Gas Wells - Samples Ordered as to Methane Content.

Table 9 presents these data in the 10 percentile variation for methane content containing the maximum number of samples. These samples indicate an enrichment of methane over domestic oil and gas well analyses.

5. Foreign Pipelines

Tables 10, 11, and 12 and figure 4 present the data available from 37 samples taken by the Bureau of Mines survey. Again, the more restricted range of methane and other hydrocarbons indicates a processing of the gas for end-use as an energy source.

6. Summary and Conclusions

The data on oil and gas wells, both foreign and domestic, indicate a wide variation in the constituents of the natural gas. This variation may prove to be less significant when individual consideration is given to placement of a liquefaction plant. The data of pipeline samples are more significant as it is believed that liquefaction plants will be constructed near pipelines to assure a continuous supply of gas. The cost of this pipeline gas will be greater due to the preliminary processing and regulation of the hydrocarbon content. Nevertheless, all groupings indicate the presence, in significant quantity, of constituents that would ultimately affect liquefaction, transport, and storage of liquefied natural gas. Table 13 presents data on some of the physical properties of the constituents, particularly their liquefaction and freezing points.

Hydrogen and helium gas are present in very small quantities in almost all gas samples. Their normal boiling points indicate they will be entirely gaseous at liquefied natural gas temperatures. These two gases have a solubility in liquid methane, but because of their low concentration it is not anticipated that this will affect the characteristics of the liquefied natural gas.

Table 9

Foreign Oil and Gas Wells

Range of Constituents for 12 Samples Having 84 - 94% Methane*

Gas (Increasing mole wt.)	Minimum mole %	Maximum mole %	Number of Samples Present
Hydrogen	Trace	0.2	3
Helium	Trace	Trace	all
Methane	84.0	94.0	all
Nitrogen	0.5	6.4	all
Ethane	2.9	6.7	all
Oxygen	0.1	0.4	5
Hydrogen Sulfide	none	none	none
Argon	Trace	Trace	6
Carbon Dioxide	Trace	0.4	11
Propane	0.6	4.0	all
n-Butane	0.2	1.4	all
Isobutane	Trace	0.8	all
n-Pentane	0.1	0.7	all
Isopentane	Trace	0.5	all
Cyclopentane	Trace	0.4	all
Hexanes +	0.2	1.0	all

* This ten percentile contains the greatest number of samples (55%).

Table 10

Foreign Pipelines

Geographical Distribution

Location	Number
Canada	23
Colombia	4
Mexico	10

Table 11

Foreign Pipelines - Summary

37 Samples

Gas (Increasing mole wt.)	Minimum mole %	Maximum mole %	Number of Samples Present
Hydrogen	Trace	0.2	24
Helium	Trace	0.53	all
Methane	47.1	96.3	all
Nitrogen	0.2	10.1	all
Ethane	0.8	15.5	all
Oxygen	Trace	1.3	18
Hydrogen Sulfide	Trace	45.4	3
Argon	Trace	0.1	31
Carbon Dioxide	Trace	5.5	all
Propane	0.1	7.2	35
n-Butane	Trace	1.8	35
Isobutane	Trace	11.3	31
n-Pentane	Trace	0.6	31
Isopentane	Trace	28.1	29
Cyclopentane	Trace	0.2	32
Hexanes +	0.1	0.5	31

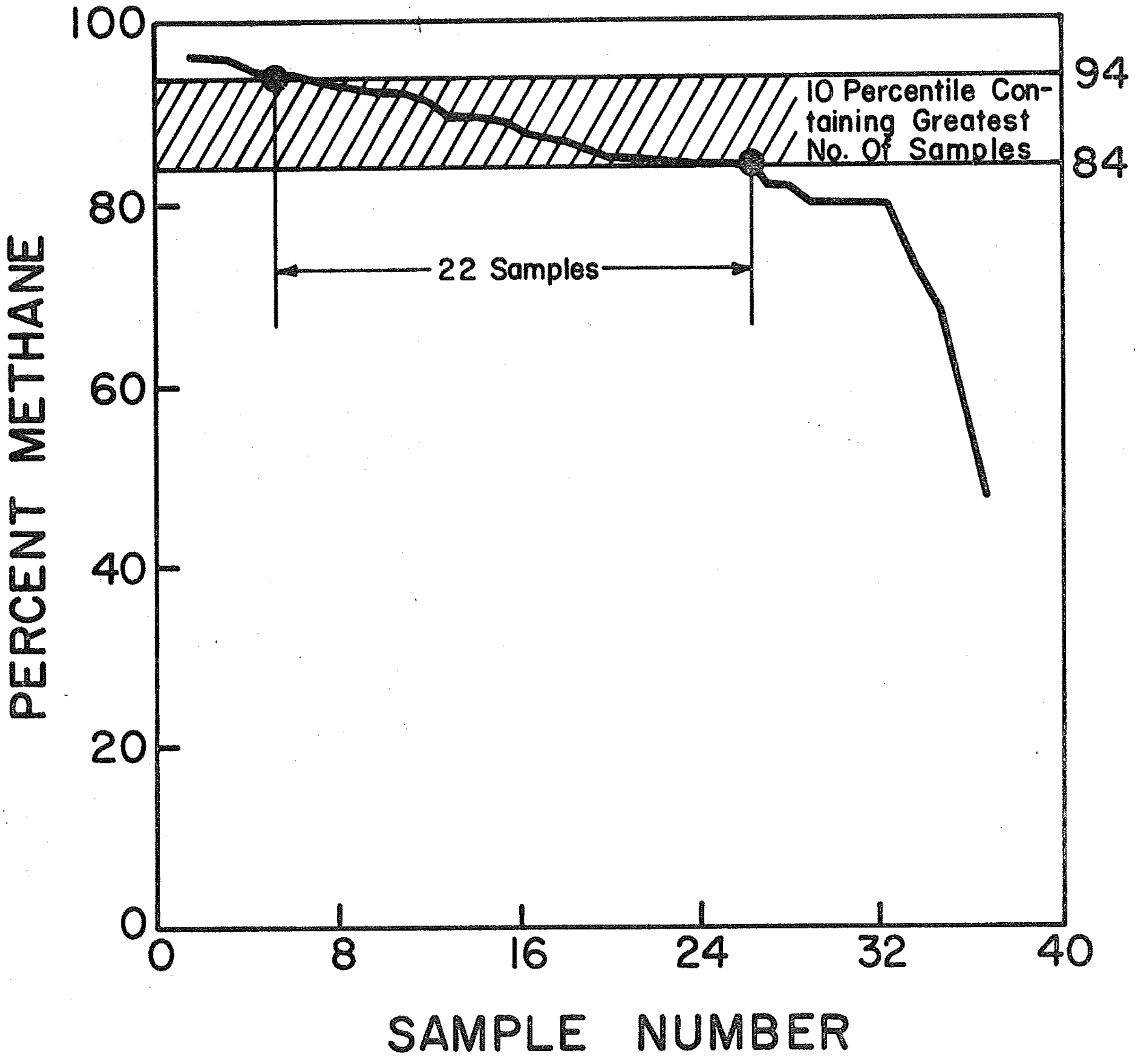

Figure 4. Foreign Pipelines - Samples Ordered as to Methane Content.

Table 12

Foreign Pipelines

Range of Constituents for 22 Samples Having 84 - 94% Methane*

Gas (Increasing mole wt.)	Minimum mole %	Maximum mole %	Number of Samples Present
Hydrogen	Trace	0.2	15
Helium	Trace	0.53	all
Methane	84.0	94.0	all
Nitrogen	0.2	6.3	all
Ethane	1.0	7.3	all
Oxygen	0.1	0.4	9
Hydrogen Sulfide	none	none	none
Argon	Trace	0.1	19
Carbon Dioxide	Trace	3.7	all
Propane	0.3	4.5	all
n-Butane	0.1	1.5	all
Isobutane	0.1	1.3	20
n-Pentane	Trace	0.6	19
Isopentane	0.1	0.5	18
Cyclopentane	Trace	0.2	19
Hexanes +	0.1	0.4	20

* This ten percentile contains the greatest number of samples (60%).

Table 13

Normal Boiling Point and Triple Point Properties of Natural Gas Constituents in the Pure State*

	Mole Wt.	NBP (K)	Triple Point (K)	Triple Point Pressure (mm Hg)
Hydrogen	2.0157	20.4	13.8	52.8
Helium	4.0028	4.21		
Methane	16.04	111.67	90.67	87.4
Nitrogen	28.016	77.36	63.15	93.5
Ethane	30.07	184.5	89.89	6×10^{-3}
Oxygen	32.00	90.18	54.4	1.14
Hydrogen Disulfide	34.08	211.4		
Argon	39.94	87.2	83.8	516.8
Carbon Dioxide	44.01	194.6 sub.	216.6	3885
Propane	44.09	231.1	85.47	4.07×10^{-6}
n-Butane	58.12	272.6	134.81	4.05×10^{-3}
Isobutane	58.12	261.4	113.56	1.52×10^{-4}
n-Pentane	72.15	309.2	143.4	4.66×10^{-4}
Isopentane	72.15	301		
Cyclopentane	70.13	322		
Hexanes +	86.17 +	342		

* This is a non-critical listing of property data and should be used for illustration purposes only.

It is not a simple matter to predict the effect of nitrogen, ethane, oxygen, or propane on the physical characteristics of liquefied natural gas. At the present time, no adequate theory is available for describing the properties of the mixtures of these liquid components. Certainly the presence of these gases in a mixture plus the small percentage of the higher boiling point hydrocarbons will have distinct effects on properties of the liquid and gaseous phases.

Problems associated with the definition of properties of liquid mixtures will persist over the entire spectrum of cryogenic usage of natural gas in liquid form. They will affect production from the standpoint of design of purification systems, heat exchangers, refrigeration and liquefaction cycles, and transfer lines to storage. In the static storage condition, selective evaporation of the components of the liquefied natural gas may present problems in predicting energy value, density, temperature and flow measurements. Finally, the design of vaporization equipment will be strongly affected by properties and characteristics of the liquefied gas mixtures.

It is not the purpose of this study to suggest solutions to these problems, but only to point out, from the basis of available analysis data, that problem areas exist and must be considered if liquefied natural gas is to achieve its projected potential.

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